THE REACTIONS OF *p*-QUINONE DIBENZENESULFONIMIDES WITH AMINES

BY

KENNETH ARTHUR SCHOWALTER

B.S., Missouri School of Mines, 1942
M.S., University of Illinois, 1949

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1951

URBANA, ILLINOIS

1951

THE REACTIONS OF *p*-QUINONE DIBENZENESULFONIMIDES WITH AMINES

BY

KENNETH ARTHUR SCHOWALTER

B.S., Missouri School of Mines, 1942
M.S., University of Illinois, 1949

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1951

URBANA, ILLINOIS

1951

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Professor Roger Adams for suggesting this research, and for his advice and encouragement throughout the investigation. He also wishes to thank the members of the staff for their advice and assistance. He is indebted to Miss E. M. Peterson for the determination and interpretation of infrared absorption spectra and to Miss Emily Davis, Miss Rachel Kopel, Mrs. Jean Fortney and Mrs. Katherine Pih for microanalytical determinations.

The author is grateful to his wife, Betty, for her faith and encouragement throughout the course of this work.

He extends his thanks to the Cincinnati Chemical Works for a fellowship held during the academic year 1949-1950.

R. UNIV.
BIBLIOTHEEK
LEIDEN

THE REACTIONS OF *p*-QUINONE DIBENZENESULFONIMIDES WITH AMIDES

Introduction

Recent investigations carried out in this laboratory have led to the discovery of a new class of compounds, the dibenzenesulfonyl, diaroyl and diacyl quinone diimides (1,2). These compounds have been found to be stable in comparison with the parent compounds, the quinone diimines. It is, therefore, possible to investigate the reactions of these nitrogen analogs of quinone and to compare those reactions with the reactions of quinone itself.

The purpose of this investigation was to study the reactions of various primary and secondary amines with the *p*-quinone dibenzenesulfonimide.

The reactions of primary and secondary aliphatic and aromatic amines and secondary aromatic-aliphatic amines were studied. Preliminary work indicated the reactions to be more complex than those with quinones and the investigation was extended to include a study of experimental procedures by which the desired products could be obtained in good yields.

Discussion Of Results

Morpholine was allowed to react with *p*-quinone dibenzenesulfonimide to yield a mixture of 2,5-dimorpholino-*p*-quinone dibenzenesulfonimide, 2,5-dimorpholino-*p*-phenylenedibenzenesulfonamide, *p*-phenylenedibenzenesulfonamide and *p*-sulfonamidophenylmorpholine. The first three products were presumably formed by a 1,4-addition mechanism, while the latter is postulated as the result of an intermediate 1,2-addition product. Further study of the reaction led to the development of a procedure for obtaining the 2,5-dimorpholino-*p*-phenylene-

dibenzenesulfonamide as the principal product. Employment of this special procedure in the piperidine reaction led to the formation of the 2,5-dipiperidino-*p*-phenylenedibenzenesulfonamide in excellent yield. The same procedure, however, with dimethylamine failed to give exclusive production of the 2,5-bis-(dimethylamino)-*p*-phenylenedibenzenesulfonamide, but instead yielded a mixture of compounds corresponding to those obtained in the morpholine reaction first discussed above.

An experimental procedure was developed for the reaction of the *p*-quinone diimide with morpholine so as to yield the 2-morpholino-*p*-phenylenedibenzenesulfonamide as the principal product. This is the first intermediate in the 1,4-addition process leading to the 2,5-dimorpholino compounds.

The 2,5-dimorpholino-*p*-quinone dibenzenesulfonimide hydrolyzed in hot dilute alkali to the 2,5-dimorpholino-*p*-quinone. The corresponding piperidino and dimethylamino compounds upon treatment with hot dilute alkali were partially hydrolyzed and partially reduced. The corresponding disubstituted-*p*-quinones, however, could not be isolated, presumably they were further hydrolyzed to the 2,5-dihydroxy-*p*-quinone.

The treatment of *p*-quinone dibenzensulfonimide with diphenylamine produced an intensely blue solution from which no crystalline compound could be obtained. The failure of the reaction was believed to be due to the low basicity of the amine and to the ease with which the diphenylamine is oxidized. Methylaniline, a slightly stronger base, reacted to yield exclusively the monoadduct, 2-methylanilino-*p*-phenylenedibenzenesulfonamide. This monoadduct could not be oxidized to the corresponding quinone diimide by any of the usual methods.

Aniline reacted with the quinone diimide, first in a 1,2 manner, to form benzenesulfonamide and *p*-quinone dianil; this then added aniline in a 1,4 manner to yield 2,5-dianilino-*p*-quinone dianil and N,N′-diphenyl-*p*-phenylenediamine. Analogous results were obtained with *p*-toluidine.

The reaction of butyl amine with the quinone diimide

yielded benzenesulfonamide and N,N′-dibutyl-*p*-quinone diimine, which polymerized to tars. By reduction of the reaction mixture, however, the N,N′-dibutyl-*p*-phenylenediamine was obtained in good yield. β-Phenylethylamine reacted in the same fashion giving, after reduction, the N,N′-di-β-phenylethyl-*p*-phenylenediamine. Ammonia reacted with the quinone diimide to yield *p*-quinone diimine which was not isolated but immediately reduced to *p*-phenylenediamine.

In contrast to *p*-benzoquinone, *p*-quinone dibenzenesulfonimide showed a greater tendency to react in the 1,2-manner. This was evidenced by the formation of the N,N′-disubstituted-*p*-quinone diimines in the reactions with primary amines. Even with the secondary amines a tendency toward 1,2-addition was indicated in the formation of *p*-sulfonamidophenylmorpholine and its dimethylamine analog. No report of this type of reaction with benzoquinone and secondary amines was found in the literature.

BIBLIOGRAPHY

1. A. S. Nagarkatti, Thesis, Doctor of Philosophy, University of Illinois, 1950.

2. J. L. Anderson, Thesis, Doctor of Philosophy, University of Illinois, 1950.

VITA

Kenneth Arthur Schowalter was born in St. Louis, Missouri, November 5, 1919. After graduating from Grover Cleveland High School in 1938 he entered the Missouri School of Mines, Rolla, Missouri. He received the degree of Bachelor of Science in Chemical Engineering from that institution in 1942. Shortly after graduation, he was called to active duty with the Corps of Engineers, U. S. Army. Upon release from active duty in January 1946, he returned to the Missouri School of Mines. He left this institution a short time later to accept a position with the Organic Research Division of Mallinckrodt Chemical Works, St. Louis, Missouri. After two years in industry the author decided to resume his graduate studies and entered the Graduate College of the University of Illinois in 1948. He received the Master of Science degree from that institution in 1949, and held the Cincinnati Chemical Works Fellowship 1949-1950.

Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41549816_0176